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Title of the invention: Drying agent, method of preparing it  
and its use

Title of the Invention

Drying agent, method of preparing it and its use

Claims

1. A drying agent comprising an A-type zeolite containing Na and K as metal cations, having the following features:

- (1) a saturation water adsorption at the temperature of 25°C and the humidity of 80% being 0.5% by weight or more;
- (2) a saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the saturation water adsorption at the temperature of 25°C and the humidity of 80%;
- (3) a saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.1% by weight or less;
- (4) an initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.015% by weight/hour or less;
- (5) a green density being 1.4 g/cm<sup>3</sup> or more; and
- (6) a compressive strength being 5.0 kg or more and a wear rate being less than 3.0%.

2. A method of preparing a drying agent as defined in Claim 1 comprising heat treating an A-type zeolite containing Na and K as metal cations or a molded product of an A-type zeolite containing Na and K as metal cations and a clay in a steam atmosphere at a moisture content of 5% by weight or more and a temperature of 600 to 750°C.

3. A method of preparing a drying agent as defined in Claim 1 comprising immersing an A-type zeolite containing Na and K as metal cations or a molded product of an A-type zeolite containing Na and K as metal cations and a clay in an alkali silicate solution and then heat treating it in a steam atmosphere at a moisture content of 5% by weight or more and a temperature of 600 to 750°C.

4. A method of drying difluoromethane (HFC32) refrigerant or a mixed refrigerant containing at least difluoromethane (HFC32) using the drying agent as defined in Claim 1.

#### Detailed Explanation of the Invention

##### (Field of the Invention)

The present invention relates to drying agents for substitute flon refrigerants. Specifically, it relates to the drying agents in refrigerating plants in which difluoromethane (HFC32) is used as the substitute flon refrigerant or a part thereof.

The term "substitute flon" collectively refers to substances capable of substituting for chlorine-containing flons which are said to deplete the ozone layer so as to damage the environment. They are chlorine-free fluorohydrocarbons consisting of hydrogen, fluorine and carbon.

Specific example of the substitute flon includes difluoromethane (HFC32), pentafluoromethane (HFC125), tetrafluoroethane (HFC134, HFC134a), trifluoroethane (HFC143,

HFC143a), difluoroethane (HFC152a), monofluoroethane (HFC161) and the like.

(Prior Arts)

Chlorine-containing flons have been widely used as refrigerants in refrigerating plants.

Recently, in view of an environmental problem of global warming due to the depletion of the ozone layer, the abolition of the chlorine-containing flons and the conversion thereof to substitute refrigerants have been contemplated. As the substitute refrigerant for the chlorine-containing flons, chlorine-free fluorohydrocarbons having a smaller ozone depletion factor become noteworthy. For example, tetrafluoroethane (HFC134a:  $C_2H_4F_2$ ) is already commercialized. Since tetrafluoroethane (HFC134a) has a poor refrigerating capacity, however, difluoromethane (HFC32:  $CH_2F_2$ ) having a higher refrigerating capacity has attracted attention in more recently.

In a refrigerating plant using a flon refrigerant, a drying agent is used for drying both the refrigerant and a refrigeration oil in the refrigerating plant.

Until now, a silica gel and a synthetic zeolite have been used as the drying agent.

On the other hand, in the refrigerating plant wherein the substitute flon refrigerant is used, a hydrophilic refrigeration oil such as glycol or ester has been used since the chlorine-free hydrofluorocarbons are hydrophilic.

The refrigeration oil is easily deteriorated by water entering from the outside of the refrigerating plant. Moist in the refrigerating plant system is iced in pipes of the refrigerating plant, by which the pipes may be clogged to give mechanical troubles to the refrigerating plant. Consequently, the importance of the drying agent in the refrigerating plant is increasing.

(Problems to be resolved by the Invention)

Difluoromethane (hereinafter abbreviated "HFC32") as a new substitute flon refrigerant has a problem that it is easily decomposed when the prior silica gel or synthetic zeolite drying agent is used. Reason therefor is believed that HFC32 is adsorbed within pores of the prior silica gel or zeolite drying agent so that the adsorbed HFC32 molecule is decomposed since HFC32 has a smaller molecular size.

Since the refrigerating plant always microvibrates during its operation, it is desirable that a drying agent used therein has a higher strength without being decomposed nor powdered by microvibrating.

(Means for Resolving Problems)

The present inventors found that as a drying agent capable of drying a refrigerant and a refrigeration oil without decomposing HFC32 in a refrigerating plant, a drying agent for the following features:

- (1) a saturation water adsorption at the temperature of 25°C and the humidity of 80% being 0.5% by weight or more;
- (2) a saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the

saturation water adsorption at the temperature of 25°C and the humidity of 80%;

(3) a saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.1% by weight or less;

(4) an initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.015% by weight/hour or less;

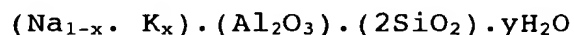
(5) a green density being 1.4 g/cm<sup>3</sup> or more; and

(6) a compressive strength being 5.0 kg or more and a wear rate being less than 3.0%;

is excellent. Also they found that the drying agent can be obtained by heat treating an A-type zeolite containing Na and K as metal cations or a molded product of an A-type zeolite containing Na and K as metal cations and a clay in a steam atmosphere with a water content of 5% by weight or more at a temperature of 600 to higher.

The drying agent of the present invention is based on a zeolite having a water adsorbability, especially an A-type zeolite containing Na and K as metal cations.

The A-type zeolite containing Na and K as metal cations is a crystalline aluminosilicate salt represented by the general formula:



wherein x is 0 to 1 and y has a value up to about 6.

The metal ions contained in the A-type zeolite of the present invention are limited to Na and K, the proportion of K relative to the sum of Na and K being preferably 33% or more. i.e. x in the above formula being 0.33 or more.

The proportion of K of 33% or more is sufficient for attaining the advantages of the present invention, although its upper limit is possibly about 99%.

The drying agent of the present invention should have a saturation water adsorption at the temperature of 25°C and the humidity of 80% of 0.5% by weight or more. If the saturation water adsorption is less than 0.5% by weight, the drying agent does not exhibit sufficient performances. The upper limit of the saturation water adsorption is not particularly limited, but it is about 30% by weight. The reason therefor is that the upper limit is 30% by weight at the K exchange proportion of 33% as is clear from the above chemical formula.

In the drying agent of the present invention, the water adsorption is increased with the increase in temperature.

In the prior drying agents, the water adsorption was decreased with the increase in temperature. For example, A3RG (trade name, ex. Tosoh Corp.) has the saturation water adsorption at the temperature of 25°C and the humidity of 80% of 20%, but at the temperature of 60°C and the humidity of 80%, its saturation water adsorption is decreased to 19%.

Whereas, in the drying agent of the present invention, the water adsorbed is hardly removed by controlling the pore size and as the result, its saturation water adsorption at the temperature of 60°C and the humidity of 80% is higher than its saturation water adsorption at the temperature of

25°C and the humidity of 80%; the former being 1.01 to 60 times, especially 1.1 to 10 times the latter.

Owing to these characteristics, the drying agent of the present invention can exhibit very excellent drying performances over the temperature range where it is used.

A method of determining the saturation water adsorption at the temperature of 25°C and the humidity of 80% comprises placing the drying agent of the present invention in an atmosphere at the temperature of 25°C and the humidity of 80%, for example in a vacuum desiccator at a saturated vapor pressure of a supersaturated aqueous ammonium chloride solution, evacuating, allowing to stand for 16 hours or more and determining the weight (A) of the drying agent having water adsorbed; then, completely dewatering the drying agent at 900°C, and determining the weight (B) of the thus-dried drying agent; and then calculating by the following equation:

$$(A-B) \times 100 / B.$$

The drying agent of the present invention should have a saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg of 0.1% by weight or less, preferably 0.06% by weight or less. The lower limit is not particularly limited, but it is preferably about 0.001% by weight. Reason therefor is that if it is less than 0.001% by weight, the drying agent does not adsorb CO<sub>2</sub> nor water, which makes it unusable as an adsorbent.

The term "saturation CO<sub>2</sub> gas adsorption" herein means the upper limit over which CO<sub>2</sub> gas is not further adsorbed



by the drying agent. Although generally it takes 8 to 16 hours to reach the saturation CO<sub>2</sub> gas adsorption, but the saturation CO<sub>2</sub> gas adsorption is defined to be a saturation level after 50 hours of adsorption in the present invention.

Since it is estimated that CO<sub>2</sub> gas has a size almost equal to or smaller than that of HFC32 considering its molecular structure, CO<sub>2</sub> gas can be used as a standard for evaluating whether or not a drying agent adsorbs HFC32 molecules.

In the prior 3A-type zeolite, its saturation CO<sub>2</sub> gas adsorption at room temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg is about 2.5% by weight.

Until now, as an A-type zeolite having less CO<sub>2</sub> gas adsorption, an ion-exchange A-type zeolite has been proposed in JP-B-48/3956 (1973).

As clear from the examples therein, however, the A-type zeolite has the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg of 0.2% by weight at minimum. Thus, the very less CO<sub>2</sub> gas adsorption as defined in the present invention has not been attained. Further, commercially available drying agents do not exhibit the performances of the present invention. For example, each of XH9 and XH600 manufactured by Union Showa k.k. has the saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg of 0.2% by weight at minimum, as described in JP-B-4/183788 (1992).

A known method of determining the saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg comprises determining a volume (volume method) or a weight (weight method) of a gas adsorbed in a predetermined weight of a drying agent. Details of these methods are fully described in "Butsuri Kagaku Jikken (Physical and Chemical Experiments)" published by Shokabo in 1968 and the like.

The drying agent of the present invention should have an initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg of 0.015% by weight/hour or less.

The lower limit of the initial CO<sub>2</sub> gas adsorption rate is not particularly limited, but it is preferably 0.001% by weight/hour. Reason therefor is that if it is less than 0.001% by weight, the drying agent does not adsorb CO<sub>2</sub> gas nor water, which makes it unusable as an adsorbent.

The term "initial CO<sub>2</sub> gas adsorption rate" herein means an adsorption rate over initial 20 hours when CO<sub>2</sub> gas is adsorbed by a drying agent at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg. It is calculated by dividing the adsorption (weight %) after 20 hours by 20 (hours).

In practice, a drying agent is used in a refrigerating plant at a temperature above room temperature (25°C), especially at a temperature ranging from 50 to 80°C. Therefore, the drying agent should have a low CO<sub>2</sub> gas adsorption rate over the above temperature range. Since the

drying agent of the present invention has the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg of 0.015% by weight/hour or less, HFC32 is less adsorbed and HFC32 is hardly decomposed even at the practical service temperature condition.

In the conventionally available drying agents such as A3RG (ex. Tosoh Corp.), the initial CO<sub>2</sub> gas adsorption rates at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg is 0.02% by weight/hour or more.

A method of determining CO<sub>2</sub> gas adsorption at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg over 20 hours is the same as the aforementioned method of determining a saturation CO<sub>2</sub> gas adsorption.

The drying agent of the present invention should have a compressive strength of 5.0 kg or more and a wear rate of less than 3.0% in order to prevent a refrigerating plant from mechanical troubles caused by fine particles resulting from cracking or wearing of the drying agent. If the compressive strength is less than 5 kg, the drying agent may be broken during use or charging.

The upper limit of the compressive strength is preferably as high as possible, but it looks to be 20 to 30 kg in the molded product of zeolite. The wear rate is preferably null.

The compressive strength means a weight by which a drying agent is broken or cracked when the load is applied thereto monoaxially. As a device for determining the

compressive strength, an autograph, a Mokuaya type hardness tester or the like is used.

The wear rate is expressed in term of the decrease (%) in weight lost by wearing after charging a drying agent in a container and shaking the container for a predetermined period. A general method for determining a wear rate is a paint shaker wet attrition method as described in JP-B-51/44111 (1976).

The wet attrition method by paint shaker comprises charging 136 ml of a hydrated drying agent and 68 ml of trichloroethylene in a 150 ml cylindrical container, shaking the container by means of a paint shaker (for example, "paint conditioner" ex. Red Devil, US) for 30 minutes and then determining the decrease in weight.

In addition, the drying agent should have a green density of  $1.4 \text{ g/cm}^3$  or more in order to improve its water adsorption, strength and wear resistance.

If the green density is less than  $1.4 \text{ g/cm}^3$ , an impact strength becomes poor and the compressive strength and wear resistance will decrease.

The upper limit of the green density is not particularly limited, but it is preferably  $1.7 \text{ g/cm}^3$  or less. Reason therefor is that if it is above  $1.7 \text{ g/cm}^3$ , the number of pores in the drying agent becomes fewer and therefore the water adsorption rate becomes slower.

The green density of the drying agent can be determined by means of a vernier micrometer or a caliper when the molded product is large or by the Archimedes method using a liquid hardly infiltrating into the molded product such as mercury or the like when the molded product is small.

For the determination of the green density by mercury, a standard mercury porosimeter is used.

The drying agent of the present invention may be zeolite itself or a zeolite product obtained by molding zeolite. Generally, a clay is used as a binder for molding.

As a clay used, a kaolin clay is exemplified. Example of the kaolin clay includes kaolin minerals, serpentine minerals, chamosite, amesite, greenalite, cronstedtite, hydrolyzed hallosite, hallosite, kaolinite, dickite, nacrite, chrysotile, antigorite, Zettritz kaolin, Cornwall kaolin, Georgia kaolin, Hongkong kaolin, Korean kaolin, Fukushu clay, Kibushi clay, Gairome clay, Seta kaolin, Iwate kaolin, Hijiori kaolin, Ibusuki kaolin, Kanpaku kaolin, or a mixture thereof.

The clay used is not necessarily limited to the kaolin clay.

The shape of the drying agent is not particularly limited. Cylinder, prism, sphere and the like can be exemplified.

And, the mixing ratio of the zeolite with the clay is not particularly limited. The ratio of the clay relative to

the zeolite is generally 1 to 40% by weight, particularly about 20 to 40% by weight.

Next, a method of preparing the drying agent of the present invention will be described below.

The drying agent of the present invention can be prepared by heating an A-type zeolite containing Na and K as metal cations or its molded product in a steam atmosphere to modify the crystal structure of the A-type zeolite resulting in contraction of the pore size thereof.

The heat treatment temperature is preferably 600°C to 800°C, particularly 650°C to 750°C. The temperature of less than 600°C is not enough for contracting the porous structure of zeolite and the temperature of above 800°C clogs the pores of zeolite completely, so that the objective drying agent of the present invention is not obtained at either temperature.

The steam concentration in the steam atmosphere is preferably 5 to 100% by weight, particularly 10 to 50% by weight in terms of a water content in the air of the heat treatment atmosphere.

A method of controlling a water concentration in the heat treatment atmosphere is not particularly limited, but a method comprising controlling a water concentration by circulating an atmospheric air in a thermostatic water bath and then supplying the atmospheric air to a zone for heating a drying agent is exemplified.

The heat treatment of zeolite in a steam is proposed in JP-B-48/3956(1973). The zeolite resulting from this method has a CO<sub>2</sub> gas adsorption at 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg of 0.2% by weight which is higher than the upper limit (0.1% by weight) defined in the present invention. Reason therefor is that a divalent cation such as Ca and the like should be present in the A-type zeolite according to the method of JP-B-48/3956(1973). In addition, JP-B-48/3956(1973) clearly describes the use of the heat treatment temperature of more than 600°C should be avoided since crystals are broken at such a temperature.

In the present invention, the metal cations in the A-type zeolite are limited to the combination of Na and K. The heat treatment of the A-type zeolite having this combination in a steam at the temperature of 600°C or more results in the modification of its crystal structure without breaking the crystal structure so that it is possible to finely control the pore size within the desired range as defined in the present invention.

Other methods for heat treating a zeolite with a steam are described in JP-B-46/5816 (1971), JP-A-54/122700 (1979) and the like. The zeolite to be heat treated in the methods is an A-type zeolite having a pore size of 4 Angstroms or more or an X-type zeolite having a pore size of 15 Angstroms or less, which are different to the zeolite of the present invention.

The heat treatment of the present invention may be carried out in any stage. It may be applied to a zeolite

itself or a product obtained by molding a zeolite with a clay.

And, the zeolite or its molded product may be immersed in an alkali silicate solution to treat its surface so that the advantage can be improved.

The nature of alkali silicate is not particularly limited, but sodium silicate and potassium silicate are generally used. It is generally used as an aqueous solution. The aqueous alkali silicate solution with a concentration of about 30% is commercially available.

If the zeolite or the molded product of zeolite and clay is immersed in an aqueous alkali silicate solution with a concentration of about 10 to about 30% for the period from several hours to 50 hours, particularly from 2 to 24 hours, the surface of the zeolite is chemically stabilized. Further the pore size of the zeolite is somewhat reduced. Thus, the pore size is more easily controlled.

A drying method using the drying agent of the present invention will be described below.

A refrigerating plant using a flon refrigerant comprises a compressor and condenser for compressing and liquefying the flon, an evaporator for gasifying the flon to cool it, a header or liquid receiver for increasing a flon concentration and accelerating the gasification of the flon, and a drier for drying the flon. According to the refrigerating method of the present invention, the drying agent of the present invention can be used by setting in the



dryer or within the liquid receiver. Fig. 1 schematically shows a diagram of the refrigerator.

The refrigerant used is HFC32 or a mixed refrigerant containing HFC32. The refrigerant to be mixed with HFC32 is not limited, but HFC125, HFC134a, HFC143a and the like can be exemplified.

A refrigeration oil used in the refrigerating plant is not particularly limited, but polyalkylene glycols, esters, mineral oils and the like can be exemplified. If necessary, any additives such as a rust preventive, an anti-oxidant and the like may be incorporated in the refrigeration oil.

Whether or not a drying agent can be used in the refrigerating plant as described above is determined by a durability test wherein the drying agent is practically used for one year or more, but it is conveniently evaluated by an accelerated test referred to as "the shield tube test". The shield tube test comprises charging 3 to 4 g of a refrigerant and 1 to 3 g of a drying agent, optionally together with 3 to 5 g of a refrigeration oil and 1 to 2 g of a metallic piece of a material usable in the refrigerating plant in a pressure-resistant sealed glass container having a capacity of about 35 ml, heating them to a predetermined temperature, allowing to stand for 14 to 30 days and then determine the decomposition of the refrigerant.

The decomposition of the refrigerant is evaluated by determining a fluorine concentration remaining in the drying agent. When the fluorine concentration remaining in the

zeolite is lower, the decomposition property of the refrigerant is evaluated to be weaker.

The decomposition of HFC32 by the drying agent of the present invention is evaluated by the shield tube test described above.

The drying agent of the present invention shows a less adsorption of CO<sub>2</sub> gas having a molecular size similar to that of HFC32 and a sufficient water adsorption. Accordingly, when it is used as a drying agent in a refrigerating plant wherein HFC32 is used as a refrigerant, it is possible to dry the refrigerant for a long period without an adsorptive decomposition of HFC32.

(Examples)

The present invention will be described by way of the following examples. These examples are not intended to limit the invention.

#### Example 1

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was immersed in an aqueous potassium silicate solution, centrifuged to remove the liquid and then dried. The thus-dried product was heat treated in an air stream with a water concentration of 15% by weight at 700°C for 5 hours, thereby yielding a drying agent.

The resultant drying agent had the features:

-- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.04% by weight;  
-- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.012% by weight/hour;  
-- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 17%;  
-- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being 18%;  
-- the green density being 1.51 g/cm<sup>3</sup>;  
-- the compressive strength as determined in Mokuya type hardness tester being 8.2 kg; and  
-- the wear rate as determined by the wet attrition method described herein being 0.1%.

Using the drying agent obtained above, the shield tube test was conducted. This test comprises charging 3 g of HFC32 and 1 g of the drying agent in a 35 ml pressure-resistant sealed glass container, then allowing to stand at 65°C for 30 days. After the test, F concentration in the drying agent was 950 ppm and HFC32 was hardly decomposed.

#### Example 2

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was immersed in an aqueous potassium silicate solution, centrifuged to remove the liquid and then dried. The thus-dried product was heat treated in an air stream with a water concentration of 30% by weight at 700°C for 5 hours, whereby a drying agent was obtained.

The resultant drying agent had the features:

- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.04% by weight;
- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.0092% by weight/hour;
- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 10%;
- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being 15%;
- the green density being 1.49 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 8.1 kg; and
- the wear rate as determined by the wet attrition method described herein being 0.1%.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 500 ppm and HFC32 was hardly decomposed.

### Example 3

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was immersed in an aqueous potassium silicate solution, centrifuged to remove the liquid and then dried. The thus-dried product was heat treated in an air stream with a water concentration of 50% by weight at 700°C for 5 hours, whereby a drying agent was obtained.

The resultant drying agent had the features:

- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.04% by weight;
- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.0062% by weight/hour;
- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 1%;
- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being 1.5%;
- the green density being 1.50 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 8.2 kg; and
- the wear rate as determined by the wet attrition method described herein being 0.1%.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 200 ppm and HFC32 was hardly decomposed.

#### Example 4

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was dried and heat treated in an air stream with a water concentration of 15% by weight at 700°C for 5 hours, whereby a drying agent was obtained. The resultant drying agent had the features:

-- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.04% by weight;  
-- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.012% by weight/hour;  
-- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 17%;  
-- the green density being 1.51 g/cm<sup>3</sup>;  
-- the compressive strength as determined in Mokuya type hardness tester being 6.0 kg; and  
-- the wear rate as determined by the wet attrition method described herein being 0.5%.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 1,050 ppm and HFC32 was hardly decomposed.

#### Example 5

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was dried and heat treated in an air stream with a water concentration of 30% by weight at 700°C for 5 hours, whereby a drying agent was obtained. The resultant drying agent had the features:

-- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.04% by weight;  
-- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.0092% by weight/hour;

- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 10%;
- the green density being 1.49 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 5.5 kg; and
- the wear rate as determined by the wet attrition method described herein being 0.5%.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 600 ppm and HFC32 was hardly decomposed.

#### Comparative Example 1

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was heat treated in an atmosphere at 650°C for 5 hours, whereby a drying agent was obtained.

The resultant drying agent had the features:

- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 2.0% by weight, i.e. the drying agent adsorbing much CO<sub>2</sub> gas;
- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.04% by weight/hour, i.e. the drying agent adsorbing CO<sub>2</sub> gas more quickly;
- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 20%;

- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being 18%;
- the green density being 1.35 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 3.5 kg; and
- the wear rate as determined by the wet attrition method described herein being 1.2%.

As clear from the above, the drying agent does not meet the following features:

- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the saturation water adsorption at the temperature of 25°C and the humidity of 80%;
- the CO<sub>2</sub> gas adsorption at 250 mmHg being 0.1% by weight or less;
- the initial CO<sub>2</sub> gas adsorption rate at 400 mmHg being 0.015% by weight/hour or less;
- the green density being 1.4 g/cm<sup>3</sup> or more; and
- the compressive strength of 5.0 kg or more, among the features as specified in Claim 1.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 1% and HFC32 was significantly decomposed.

#### Comparative Example 2

A3RG (trade name) was commercially available from Tosoh Corp. as a drying agent for HFC134a. It has the features:

- the CO<sub>2</sub> gas adsorption at 25°C and 250 mmHg being 1.8% by weight;



- the initial CO<sub>2</sub> gas adsorption rate at 75°C and 400 mmHg being 0.048% by weight/hour;
- the saturation water adsorption at 25°C and the humidity of 80% being 20%;
- the saturation water adsorption at 60°C and the humidity of 80% being 19%;
- the green density being 1.5 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 8.0 kg; and
- the wear rate as determined by the wet attrition method described herein being 0.1%.

As clear from the above, the drying agent does not meet the following features:

- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the saturation water adsorption at the temperature of 25°C and the humidity of 80%;
- the CO<sub>2</sub> gas adsorption at 250 mmHg being 0.1% by weight or less; and
- the initial CO<sub>2</sub> gas adsorption rate at 400 mmHg being 0.015% by weight/hour or less,

among the features as specified in Claim 1.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 2% and HFC32 was significantly decomposed.

### Comparative Example 3

Following the procedures of Example 4 of JP-B-48/3956(1973), a drying agent having the features:

-- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and 250 mmHg being 0.2% by weight; and  
-- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 21.3%;  
was prepared.

The above drying agent has the features:  
-- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and 400 mmHg being 0.025% by weight/hour;  
-- the saturation water adsorption at 60°C and the humidity of 80% being 20%;  
-- the green density being 1.5 g/cm<sup>3</sup>;  
-- the compressive strength as determined in Mokuya type hardness tester being 6.0 kg; and  
-- the wear rate as determined by the wet attrition method described herein being 1%.

The drying agent does not meet the following features:  
-- the saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the saturation water adsorption at the temperature of 25°C and the humidity of 80%;  
-- the CO<sub>2</sub> gas adsorption at 250 mmHg being 0.1% by weight or less; and  
-- the initial CO<sub>2</sub> gas adsorption rate at 400 mmHg being 0.015% by weight/hour or less,  
among the features as specified in Claim 1.

Using the drying agent obtained above, the shield tube test was conducted in the same way as described in Example 1. After the test, F concentration in the drying agent was 2% and HFC32 was significantly decomposed.

#### Comparative Example 4

70 % by weight of an A-type zeolite containing Na and K (1:1) as metal cations was kneaded with 30% by weight of a domestic kaolin clay and the mixture was granulated to obtain a spherical molded product having 2 mm in diameter. Then the molded product was immersed in an aqueous potassium silicate solution, centrifuged to remove the liquid and then dried. Then, the thus-dried product was heat treated in an air stream with a water concentration of 15% by weight at 600°C for 5 hours, whereby a drying agent was obtained.

The resultant drying agent had the features:

- the CO<sub>2</sub> gas adsorption at the temperature of 25°C and 250 mmHg being 0.04% by weight; -- the initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and 400 mmHg being 0.012% by weight/hour;
- the saturation water adsorption at the temperature of 25°C and the humidity of 80% being 20%;
- the saturation water adsorption at the temperature of 65°C and the humidity of 80% being 19%;
- the green density being 1.30 g/cm<sup>3</sup>;
- the compressive strength as determined in Mokuya type hardness tester being 5.0 kg; and
- the wear rate as determined by the wet attrition method described herein being 3.2%.

The drying agent obtained above was significantly powdered when subjected to the wet attrition test. Thus, its wear strength was not enough for use as a drying agent in a refrigerator where the vibration occurs.

(Effect of the Invention)

The drying agent of the present invention has a higher water adsorption, a less CO<sub>2</sub> gas adsorption, a higher compressive strength and a lower wear rate, when compared with those of the prior zeolite adsorbent. Owing to these advantages, the drying agent of the present invention is suitable as a drying agent, especially for a difluoromethane refrigerant.

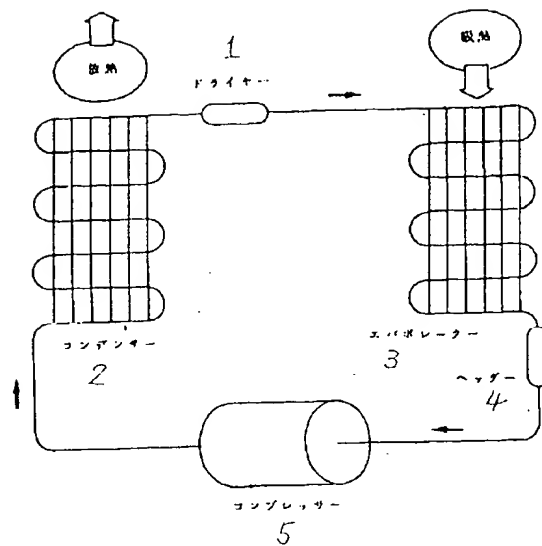
Brief Explanation of Drawing

Fig. 1 shows an embodiment of a refrigerating plant using the adsorbent of the present invention.

Fig. 1

exothermic

endothermic



- 1 drier
- 2 condenser
- 3 evaporator
- 4 header
- 5 compressor

## Abstract

### (Constitution)

A drying agent comprising an A-type zeolite containing Na and K as metal cations, having the following features:

- (1) a saturation water adsorption at the temperature of 25°C and the humidity of 80% being 0.5% by weight or more;
- (2) a saturation water adsorption at the temperature of 60°C and the humidity of 80% being higher than the saturation water adsorption at the temperature of 25°C and the humidity of 80%;
- (3) a saturation CO<sub>2</sub> gas adsorption at the temperature of 25°C and the CO<sub>2</sub> gas partial pressure of 250 mmHg being 0.1% by weight or less;
- (4) an initial CO<sub>2</sub> gas adsorption rate at the temperature of 75°C and the CO<sub>2</sub> gas partial pressure of 400 mmHg being 0.015% by weight/hour or less;
- (5) a green density being 1.4 g/cm<sup>3</sup> or more; and
- (6) a compressive strength being 5.0 kg or more and a wear rate being less than 3.0%,  
a method of preparing it and a method of drying a difluoromethane (HFC32) refrigerant and a mixed refrigerant containing at least difluoromethane (HFC32) using the drying agent.

### (Effect)

The drying agent of the present invention has a higher water adsorption, a less CO<sub>2</sub> gas adsorption, a higher compressive strength and a lower wear rate, when compared with those of the prior zeolite adsorbent. Owing to these advantages, the drying agent of the present invention is

suitable as a drying agent, especially for a difluoromethane refrigerant.